UDC 543.544.6

SEPARATION OF COPPER, ZINC AND CADMIUM ON A MIXED ION-EXCHANGE COLUMN

混合イオン交換カラムによる銅，亜鉛，カドミウムの分離

by Takeo YAMABE*
山 辺 武 郎

1. Introduction

In ion-exchange columns there are two types of columns, single column and mixed column. The single column contains only the cation-exchange resin or the anion-exchange resin, and the mixed column contains both the cation-and anion-exchange resins. However only the single column was usually used so far. We used the mixed column for the group separation of amino acid for the first time[1], but we did not yet hear the investigations to use the mixed column for ion-exchange separation. In this paper we will discuss the availability of mixed column for metal ion separation, and show that the separation of copper, zinc and cadmium can be carried out by use of an useful eluent.

2. Experimental

(1) Preparation of Mixed Column

Cation- and anion-exchange resins used are respectively strongly acidic and strongly basic (Diaion), and were conditioned with hydrochloric acid and sodium hydroxide solution as usual. The proper quantities of both resins were mixed, not in pure water but in the concentrated electrolyte solution such as 20% sodium chloride solution, because a violent aggregation will occur in pure water. As the eluent is hydrochloric acid in this experiment, it is not necessary to backwash the column before regeneration.

* Dept. of Industrial Chemistry and Metallurgy, Inst. of Industrial Science, Univ. of Tokyo.

(2) Column Operation and Determination of Metal Ion

Total resin quantities in the column are 10.8 ml (resin length in column = 17 cm), and 200 μl of each 1/4 M metal ion solution ($CuCl_2$, $ZnCl_2$, $CdCl_2$) are added in the upper part of the column. The eluents are passed through the column at rate 1 ml/min., and the eluates are fractioned by fraction collector.

Copper, zinc and cadmium concentration are determined by chelate titration method with $M/100$ EDTA solution.

Each metal ion in the fraction developed from mixed solution is determined, after the qualitative determination with Hitachi UHF Plasma Spectra Scan Apparatus (Model 300).

3. Results and Discussion

(1) Discussion of Elution Curve

In the elution curve, the following relation holds

$$Vm(A) = Vs + Kd(A) \cdot V_R \qquad (1)$$

where $Vm(A)$ is the peak volume, the eluate volume up to the maximum concentration of ion A, Vs, V_R are respectively the interstitial water and the resin volume, and $Kd(A)$ is the distribution coefficient of ion A in case ion A is minute component.

Similary for another minute component ion B, the following relation holds.

$$Vm(B) = Vs + Kd(A) \cdot V_R \qquad (2)$$

Therefore, in order to discuss the separability between ion A and ion B, we compare Vm(A) with Vm(B) and on the same column, we can compare $Kd(A)$ with $Kd(B)$ in place of the peak volume [$Vm(A)$ and $Vm(B)$].

Then if we consider the peak base width, $w(A)$ and $w(B)$, the base width in the elution curve at the point of maximum concentration, we can define the resolution (R), the separability of ion A from ion B, as the following relation.

$$R=\frac{2[Vm(B)-Vm(A)]}{w(A)+w(B)} \quad (3)$$
$$[Vm(B)>Vm(A)]$$

When separation is complete, $R\geqq1$, and when separation is incomplete, $1>R>0$.

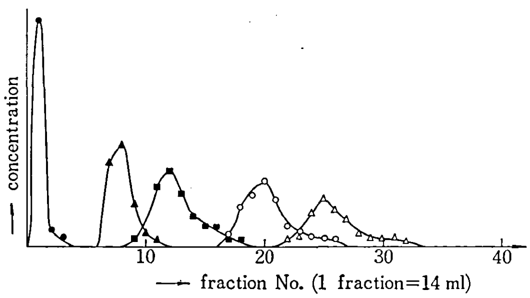
(2) **Types of Elution Behaviors**

The elution behaviors of metal ion solution were examined in the single columns or the mixed columns. As the results of these elution experiments, we can classify these elution behaviors of metal ions in the following three types.

(i) Type I.

For the single column of anion-exchange resin, Kd is very small, and for the single column of cation-exchange resin, Kd is very large. For the mixed column, Kd is between those of the upper two columns, corresponding to the mixed ratios of both resins.

In Type I, the metal ion exists almost exclusively as cation. Fig. 1 is the example of Type I.



Column: △ single column (cation-exchange resin)
○ mixed column (cation 2 : 1 anion)
■ mixed column (cation 1 : 1 anion)
▲ mixed column (cation 1 : 2 anion)
● single column (anion-exchange resin)

Fig. 1 Elution behavior of Cu^{2+} with eluent of 0.5 N HCl.

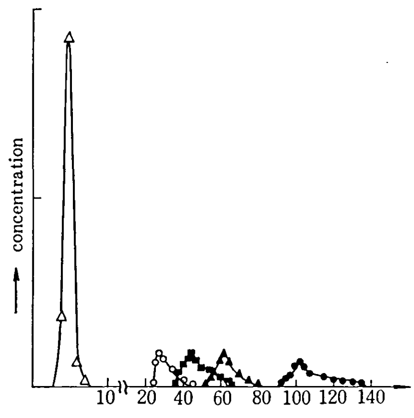
Elution conditions belonging to Type I are shown by metal ion and eluent; Cu, 0.25 N HCl, 0.5 N HCl; Zn, 0.25 N HCl.

(ii) Type II

Contrary to Type I, for the single column of cation-exchange resin, Kd is small, and for the single column of anion-exchange resin, Kd is very large. Again, for the mixed column, Kd is between those of the upper two columns, corresponding to the mixed ratios of the both resins.

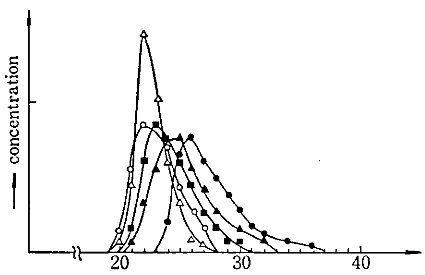
In Type II, the metal ion exists almost exclusively as complex anion. Fig. 2 is the example of Type II. Elution conditions belonging to Type II are shown by metal ion and eluent; Zn, 1 N HCl; Cd, 0.25 N HCl, 0.5 N HCl.

(iii) Type III



Column: △ single column (cation-exchange resin)
○ mixed column (cation 2 : 1 anion)
■ mixed column (cation 1 : 1 anion)
▲ mixed column (cation 1 : 2 anion)
● single column (anion-exchange resin)

Fig. 2 Elution behavior of Zn^{2+} with eluent of 1 N HCl



Column: △ single column (cation-exchange resin)
○ mixed column (cation 2 : 1 anion)
■ mixed column (cation 1 : 1 anion)
▲ mixed column (cation 1 : 2 anion)
● single column (anion-exchange resin)

Fig. 3 Elution behavior of Zn^{2+} with eluent of 0.5 N HCl.

In Type III, the elution behaviors of both the single columns and the mixed columns of different mixed ratios show almost same *Kd*.

In Type III, the metal ion exists as cation and complex anion in almost the same degree. Fig. 3 is the example of Type III. Elution conditions belonging to Type III are shown by metal ion and eluent; Cu, 1 N HCl; Zn 0.5 N HCl.

(3) Estimation of Separability

Although the separability is shown with the resolution (*R*) in the equation (3), we must avoid the elution behavior of too small *Kd* and too large *Kd*. If *Kd* is too small, the elution operation becomes difficult, and if *Kd* is too large, tailing will occur.

In Type I and Type II, there are many cases where the single columns behave too small *Kd* and too large *Kd*, for the definite eluent. In such cases we must adopt the mixed column of the proper mixed ratio in order to obtain the available *Kd*.

In Type III, we can adopt any columns, and then we must determine the availability due to another factor.

(4) Separation of Copper, Zinc and Cadmium

At last, we will show the case where the mixed column is the most useful.

Fig. 4 shows the elution behaviors of Cu, Zn and Cd by use of (1 : 1) mixed column with the eluent of 0.5 N HCl, in case of single component or mixture.

In case of mixture, a little interaction of other components exist in the elution curve, but the elution behavior and the separability of three components were the almost same as the single component. Therefore we can consider the separability of mixture from the comparison with the elution behavior of single component.

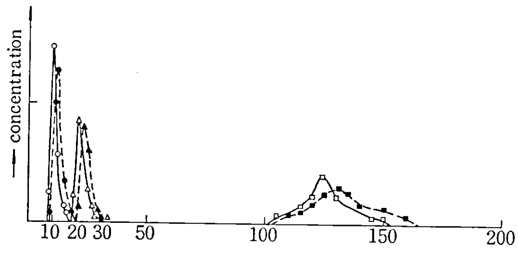


Fig. 4 Separation of Cu, Zn and Cd by mixed column.

4. Conclusion

(1) When the eluent is fixed, the most separable conditions can be obtained with the mixed column of the various mixed ratios of cation-exchange resin and anion-exchange resin in certain cases.

(2) We can obtain the good result in the case of the separation of Cu, Zn and Cd and the eluent of 0.5 N HCl. However we also believe in the existences of many such cases.

(Manuscript received June 30, 1972)

References

1) Takeo YAMABE, Kazuko YAMAGATA, and Manabu SENŌ. Nippon Kagaku Zasshi **89**, 772 (1968).